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(54) Title: **ION CONDUCTING COMPOSITE MEMBRANE MATERIALS CONTAINING AN OPTIONALLY MODIFIED ZIRCONIUM PHOSPHATE DISPERSED IN A POLYMERIC MATRIX, METHOD FOR PREPARATION OF THE MEMBRANE MATERIAL AND ITS USE**

(57) Abstract: The invention provides composite membrane materials comprising a polymer of the state of art uniformly filled with a zirconium phosphate, preferably α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate particels. The composite membrane materials are preferably prepared starting from a solution of a polymer of the state of art and from a colloidal dispersion of α -zirconium phosphate or a zirconium phosphate sulfoarylenphosphonate. The colloidal particles are transferred into the solution of the polymer preferably by mixing the dispersion with the solution or by means of phase transfer. The membrane material is preferably obtained by removing the solvent by evaporation or by a suitable non-solvent. Besides the composite membrane materials and the preparation methods, the use of the above membrane materials is claimed as ionomeric membranes with high overall performance in high temperature, especially hydrogen, and in indirect methanol fuel cells and with decreased methanol crossover in direct methanol fuel cells.

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allowing hydrogen produced by reforming of alkanols or hydrocarbons to be used as a fuel. Finally, Nafion membranes exhibit high permeability to methanol; therefore they cannot be used in "direct" methanol FC.

- 5 The problem to obtain polymeric proton conducting membranes combining good mechanical properties with low methanol permeability and/or high proton conductivity above 70-80 °C can be overcome with at least two different strategies: 1) synthesis of new ionomers possessing the desired properties, 2) improvement of properties of ionomers of the
- 10 state of art by adding inorganic particles which are able to reduce the membrane permeability to methanol, owing to their shape and size, and/or to facilitate (or even increase) the ionomer hydration above 80 °C, owing to their hydrophilic character.
- 15 As far as the second strategy is concerned, according to the patent USA 5, 523, 181, an improvement of humidification of perfluorocarboxysulfonic membranes can be obtained by dispersing particles of silica gel in the above membranes. This modification allows the fuel cell to be operated at reduced relative humidity although at
- 20 temperature below 100 °C. Higher working temperatures can be achieved with a suitable thermal treatment of the silica modified membrane according to the patent EP 0 926 754.

Furthermore, according to the international patent WO96/29752, the

25 permeability to methanol is indeed reduced by adding inorganic particles among which, in particular, zirconium phosphate. Relatively to the problem of an excessive methanol permeability, the recent industrial success in the preparation of nanopolymers filled with organophilic clays clearly indicated that the presence of lamellar particles can decrease to

30 a great extent the gas permeability of the polymeric matrix. This is a consequence of the fact that, during the extrusion process, the lamellar particles tend to orientate themselves parallel to the membrane surface.

It is known from the literature (G. Alberti, M. Casciola, U. Costantino, A. Peraio, E. Montoneri, Solid State Ionics 50 (1992) 315; G. Alberti, L. Boccali, M. Casciola, L. Massinelli, E. Montoneri, Solid State Ionics 84 (1996) 97) that some α - or γ -layered zirconium phosphate sulfoarylenphosphonates exhibit proton conductivity up about 0.1 S cm^{-1} . These compounds are represented by the general formulae $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $0 < x \leq 2$ (α -type compounds), or $\text{Zr}(\text{PO}_4)(\text{O}_2\text{P}(\text{OH})_2)_{1-x}(\text{HO}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $0 < x \leq 1$ (γ -type compounds), where Ar is an arylsulfonated group. The inventors have recognised that these compounds must be considered more hydrophilic than silica due to the super acidic character of the sulfonic function.

Powders of amorphous zirconium phosphate metasulfophenylenphosphonates of composition $\text{Zr}(\text{O}_3\text{POH})_{2-x}(\text{O}_3\text{P-Ar})_x \cdot n\text{H}_2\text{O}$, with $x=1$ and 1.5, supported by sulfonated poly-ether-ether-ketone were already used for the preparation of composite membranes containing 40 % proton conductor without any loss of the ionomer conductivity (E. Bonnet, D.J. Jones, J. Rozière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, B. Bauer, A. Peraio, E. Ramunni, J. New Mat. Electrochem. Systems, 3 (2000) 87). Similar results were also obtained for Nafion 1100 membranes loaded with powder of an α -titanium phosphate metasulfophenylenphosphonate up to 20 % (G. Alberti, U. Costantino, M. Casciola, S. Ferroni, L. Massinelli, P. Staiti, Solid State Ionics 145 (2001) 249).

It was now surprisingly found that both amorphous and α - or γ -layered zirconium phosphate as well as zirconium phosphate metasulfoarylenphosphonates form stable colloidal dispersions in some organic solvents (e.g. N, N'-dimethylformamide (DMF), N-methyl-2-

modified zirconium phosphate, especially zirconium phosphate sulfoarylenphosphonate, containing membrane material is $>10^{-2} \text{ S cm}^{-1}$ at 70 °C and 95 % relative humidity.

- 5 It is a further object of the present invention to provide a composite membrane material made of an ionomer of the state of art filled with well-dispersed lamellar particles of α -zirconium phosphate of controlled thickness and surface.
- 10 It is a further object of the present invention to provide a procedure for the preparation of a composite membrane material made of the said ionomer and of a zirconium phosphate, preferably a layered zirconium phosphate, especially α -zirconium phosphate, or of a zirconium phosphate sulfoarylenphosphonate, starting from a solution of the
- 15 ionomer and from a colloidal dispersion of α -zirconium phosphate or of the said zirconium phosphate sulfoarylenphosphonate.

The invention concerns in one aspect the preparation of a colloidal dispersion of α -zirconium phosphate or of a proton conducting zirconium

20 phosphate sulfoarylenphosphonate in a suitable solvent or mixture of solvents, and in the subsequent transfer of the colloidal particles into a solution of a polymer, especially an ionomer, of the state of art. The mixture thus obtained is cast on the surface of a smooth plane support and the solvent is removed by heating or by using a suitable non-

25 solvent. Transfer of the colloidal particles into the polymer, especially ionomer, solution can be carried out (1) by mixing the polymer, especially the ionomer, solution with the colloidal dispersion or (2) by means of "phase transfer". It is possible to use noncharged polymers as conductivity is contributed by the zirconium phosphate. Preferably there

30 are used ionomers, especially sulfonated polymers due to their conductivity at low temperatures ($<100 \text{ }^{\circ}\text{C}$). There can be used

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Crystalline zirconium phosphate material is suitable for direct methanol fuel cells with diameters of 1-10 μm .

5 The thickness of the zirconium phosphate and zirconium phosphate sulfoarylenphosphonate dies ranges in the scale of single molecule layers. The overall thickness of the composite membranes is between 10 μm and 100 μm , preferably 30-60 μm .

10 An object of the invention are preferably also membranes comprising the composite membrane material for fuel cells or in fuel cells.

Another object of the invention are further fuel cells comprising the composite membrane material.

15 The following examples have the purpose of facilitating the understanding of the invention, and do not intend to limit in any manner its scope, which is solely defined by the appended claims.

20 Figure 1 shows the orientation of particles in the composite membrane material

Figure 2 shows conductivity behaviour of PFSA + 3 % ZrP

Figure 3 shows conductivity of PPEK + 20 % ZrP

Figure 4 shows polarisation curve of s-PEEK + 20 % ZrP compared to Nafion 117

25 Figure 5 shows conductivity behaviour of PFS-Li + 10 % ZrSPP

Figure 6 shows an 20.000x magnification of s-PEK + 20% Zr(SPP)_{1.3}

Figure 7 shows an 10.000x magnification of s-PEK + 10% Zr(SPP)_{1.3}

Figure 8 shows conductivity of s-PEK + 20 % ZrSPP

Figure 9 shows conductivity of s-PEKK + 20 % ZrSPP

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ionomer solution in DMF with a colloidal dispersion of the zirconium phosphate sulfophenylenphosphonate in the same solvent.

a) Preparation of $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$

- 5 7.5 ml of 1M H_3PO_4 and 15 ml of 1M metasulfophenylenphosphonic acid are mixed and concentrated by heating overnight at 80 °C. The dense solution thus obtained is mixed with 50 ml of acetonitrile and water is added until a clear solution is obtained. 13.6 ml of an aqueous solution of 0.75M ZrOCl_2 are then added drop wise to the acetonitrile solution.
- 10 The white precipitate thus formed is held under vigorous stirring for half an hour and washed two times with 2M HCl (2 x 50 ml) and two times with acetonitrile (2 x 50 ml). The slurry, obtained after centrifugation at 3000 rpm, is used for the preparation of a colloidal dispersion in DMF.

- 15 b) Preparation of a colloidal dispersion of $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$ in DMF

A weighed amount of the above slurry is mixed with an equal amount of DMF and stirred overnight. The mixture is left at rest for one day to allow sedimentation of the solid. The supernatant colloidal dispersion contains

20 9 % $\text{Zr}(\text{O}_3\text{POH})_{0.6}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.4}$, 50 % DMF and 41 % acetonitrile.

c) Membrane material preparation

- A weighed amount of s-PEK1.3 (corresponding to 1.2 g of anhydrous ionomer) is dissolved under vigorous stirring in 8 g of NMP at 130 °C.
- 25 Subsequently, 3.37 g of the colloidal dispersion described in b) are mixed with 9.05 g of the s-PEK1.3 solution. This mixture is held under stirring for half an hour and then cast on a glass plate. The solvent is evaporated as indicated in example 1. The membrane material thus obtained (thickness 0.05 mm, 20 % of inorganic material) is kept in
- 30 water.

phase product obtained is cast on a glass support and the resulting film dried as described in example 1.

The conductivity of a membrane material containing 10 % of inorganic material at 100 °C and 80 % relative humidity is $1.3 \cdot 10^{-3} \text{ S cm}^{-1}$.

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EXAMPLE 4

Preparation of a perfluorosulfonic acid (PFSA) hybrid membrane for medium temperature fuel cells containing 3 wt. % of amorphous
10 α -zirconium phosphate (ZrP)

29,12 g of a 10 wt.% solution of the Li-form of the perfluorosulfonic acid polymer PFSA (Nafion®, EW 1150) in N-methyl-2 pyrrolidone (NMP) and 1,2 g of a 10 wt.% gel of amorphous exfoliated ZrP in NMP/H₂O are
15 mixed by carefully adding the colloidal dispersion of exfoliated ZrP in small quantities under vigorous stirring into the PFS-Li solution. After filtration of the mixture through a 10 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10mm/s).

20 After applying following drying protocol and delamination from the glass plate, a film of 50-60 μm thickness is obtained.

Drying protocol: 30 min at 50 °C, then 30 min at 60 °C, then 30 min 80 °C, then 30 min 120 °C

Before further characterisation, the film was carefully conditioned in
25 1M H₂SO₄, then repeatedly washed in demineralised water until neutral pH was obtained.

The following conductivity behaviour (figure 2) was obtained in a temperature controlled measuring cell under full humidification.

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small quantities under vigorous stirring into the s-PEEK solution. After filtration of the mixture through a 40 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10 mm/s).

- 5 After applying following drying protocol and delamination from the glass plate, a film of 50-60 μm thickness is obtained.

Drying protocol: 30 min at 60 °C, then 30 min at 80 °C, then 30 min 80 °C, then 30 min 120 °C

- Before further characterisation, the film was carefully conditioned in
10 1M H_2SO_4 , then repeatedly washed in demineralised water until neutral pH was obtained.

- The following polarisation curve (figure 4) was obtained compared to a
Nafion117 film from Dupont, in a single cell (20 cm^2) at 80 °C under
15 DMFC (direct methanol fuel cell)-conditions: Anode 1 Mol/l methanol in water. Cathode O_2 . Electrodes: Anode: 2,4 mg/cm^2 Pt/Ru; Cathode: 3 mg/cm^2 Pt.

20 EXAMPLE 7

Preparation of a perfluorosulfonic acid (PFSA) hybrid membrane for medium temperature fuel cells containing 10 wt. % of zirconium phosphate sulfophenylenphosphonate (ZrSPP)

- 25 1g ZrSPP is solubilised in 10 ml H_2O . 20 ml NMP is added and the mixture is reduced in volume to 61 % at 80 °C. A clear solution is obtained. 25 g of a 10 wt.% in NMP solution of the Li-form of the perfluorosulfonic acid polymer PFSA (Nafion®, EW 1150) and 6 g of the afore mentioned ZrSPP solution is mixed by carefully adding the ZrSPP-
30 solution in small quantities under vigorous stirring. After filtration of the mixture through a 40 μm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 μm , feed rate: 10 mm/s).

Before further characterisation, the film was carefully conditioned in 1M H₂SO₄, then repeatedly washed in demineralised water until neutral pH was obtained.

- 5 The following conductivity (figure 8) was obtained at reduced humidity (90 %). The reference measurement is given as s-PEK.

EXAMPLE 9

- 10 Preparation of a sulfonated polyetherketoneketone (s-PEKK) hybrid membrane for direct methanol fuel cells containing 20 wt. % of crystalline zirconium phosphate sulfophenylenphosphonate (ZrSPP)

- 30,22 g of a 10 wt. % in NMP solution of the polyetherketoneketone (PEKK) polymer (equivalent weight: 775 g/equivalent) and 10,78 g of a 7 wt. % gel of amorphous exfoliated ZrSPP in DMF/ H₂O is mixed by carefully adding the ZrSPP-gel in small quantities under vigorous stirring into the PEKK solution.

- After filtration of the mixture through a 40 µm filter, a film is prepared on a glass plate using a doctor blade (gap: 600 µm, feed rate: 10mm/s).

After applying following drying protocol and delamination from the glass plate, a film of 50-60 µm thickness is obtained.

- Drying protocol: 30 min at 60 °C, 30 min at 80 °C, then 60 min 120 °C

The following conductivity (figure 9) was obtained in 0,5 Mol NaCl and flux of methanol was measured in a diffusion cell applying a feed concentration of 5 Mol/l CH₃OH versus demineralised water at 50 °C.

8. The membrane material according to one of the preceding claims wherein the polymeric matrix of the membrane material is at least one synthetic ionomer of the group consisting of perfluorosulfonic polymers, sulfonated polyvinylidenefluoride, sulfonated polyetherketones, sulfonated polybenzimidazoles, sulfonated polyphenylsulfones, sulfonated polysulfones and sulfonated polyethersulfones.

9. The membrane material according to one of the claims 2 and 4-8 wherein the zirconium phosphate sulfoarylenphosphonate contains specifically one or more phosphonate groups bonded to the zirconium atom.

10. The membrane material according to one of the claims 2 and 4-9 wherein the sulfoarylenphosphonate group is meta-sulfophenylenphosphonate.

11. The membrane material according to one of the preceding claims wherein optionally modified zirconium phosphate is of layered type.

12. The membrane material according to one of the preceding claims wherein the amount of optionally modified zirconium phosphate in the membrane material is 0,5 % – 70 %, preferably 5 % - 40 %, especially 10 % - 25 % by weight.

13. A method for the preparation of the proton conducting composite membrane material according to one of claims 1-12 based on the following steps:

a) preparation of a layered zirconium phosphate or modified zirconium phosphate,

phosphate or modified zirconium phosphate is obtained by mixing the ionomer solution with the colloidal dispersion of the layered α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate.

5 17. The method for the preparation of the proton conducting composite membrane material according to one of claims 13-16 wherein the colloidal dispersion of the α -zirconium phosphate or modified zirconium phosphate is obtained by using organic solvents selected from N, N'-dimethylformamide, N-methyl-2-pyrrolidone, dimethylsulfoxide,
10 acetonitrile and alkanols, preferably N, N'-dimethylformamide and/or N-methyl-2-pyrrolidone, or their mixtures or water or mixtures of water and organic solvent.

18. The methods for the preparation of the proton conducting
15 composite membrane materials of one of claims 13-17 wherein the ionomer solution and the colloidal dispersion are prepared in the same solvent or in different solvents, provided that the mixing of the solution with the dispersion does not cause colloid flocculation or ionomer precipitation.

20 19. The method for the preparation of the proton conducting composite membrane material according to claims 13-18 wherein the mixture containing the ionomer and the layered α -zirconium phosphate or zirconium phosphate sulfoarylenphosphonate is obtained by "phase
25 transfer".

20. The methods for the preparation of the proton conducting composite membrane materials according to claims 13-18 wherein the solvent is removed from the polymer-colloid mixture by evaporation.

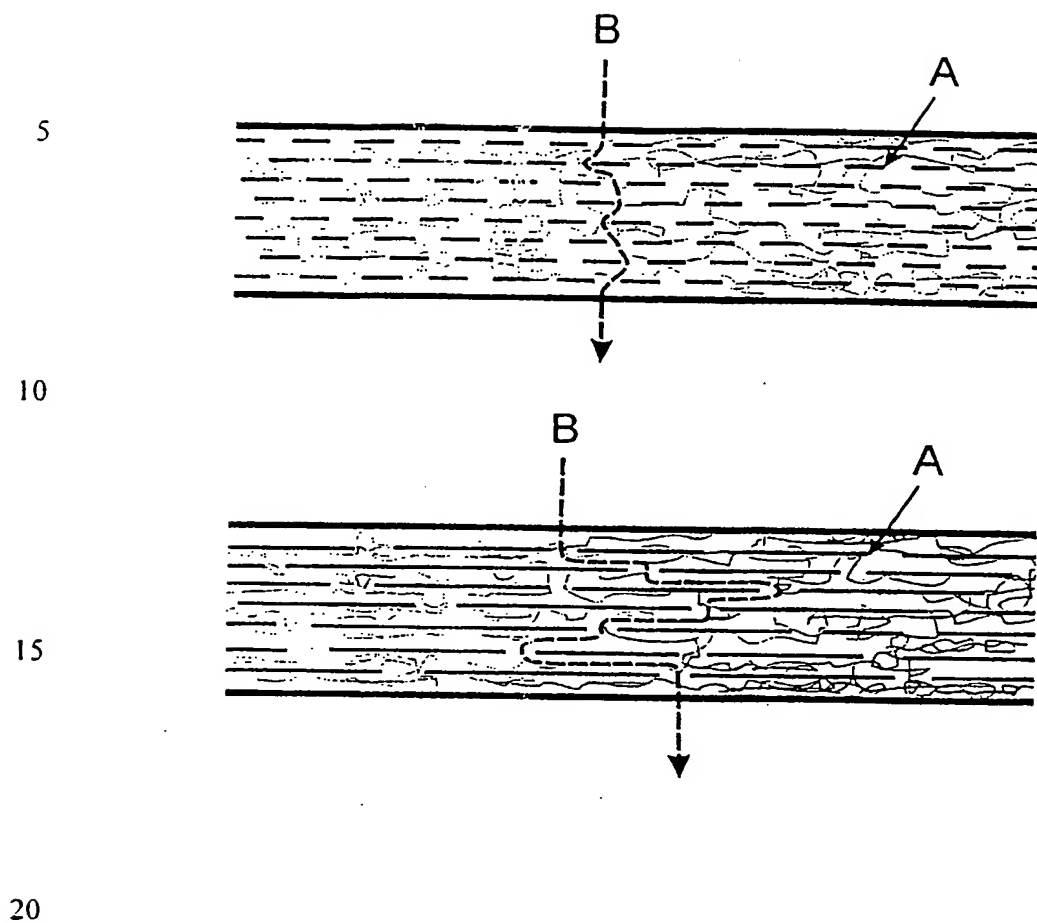
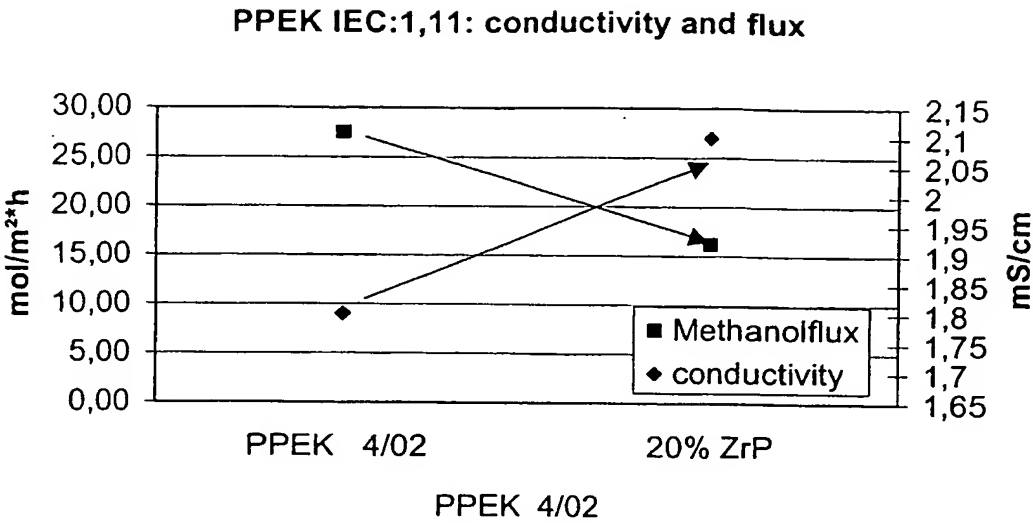
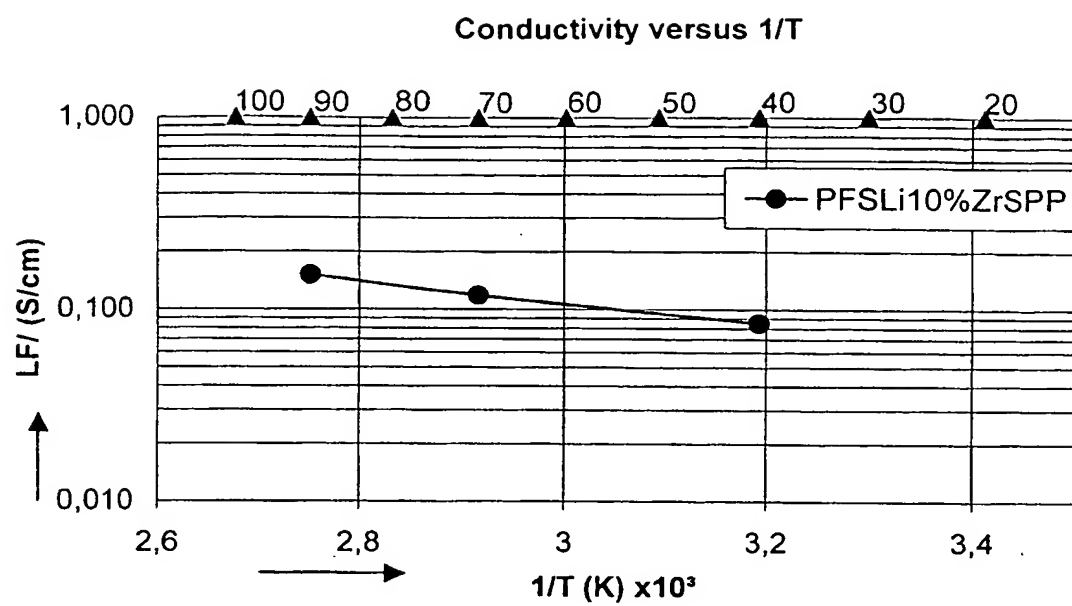


Figure 1

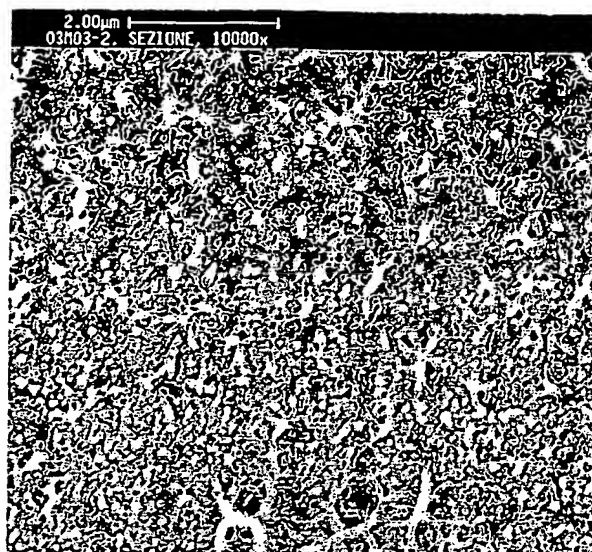


5 Figure 3

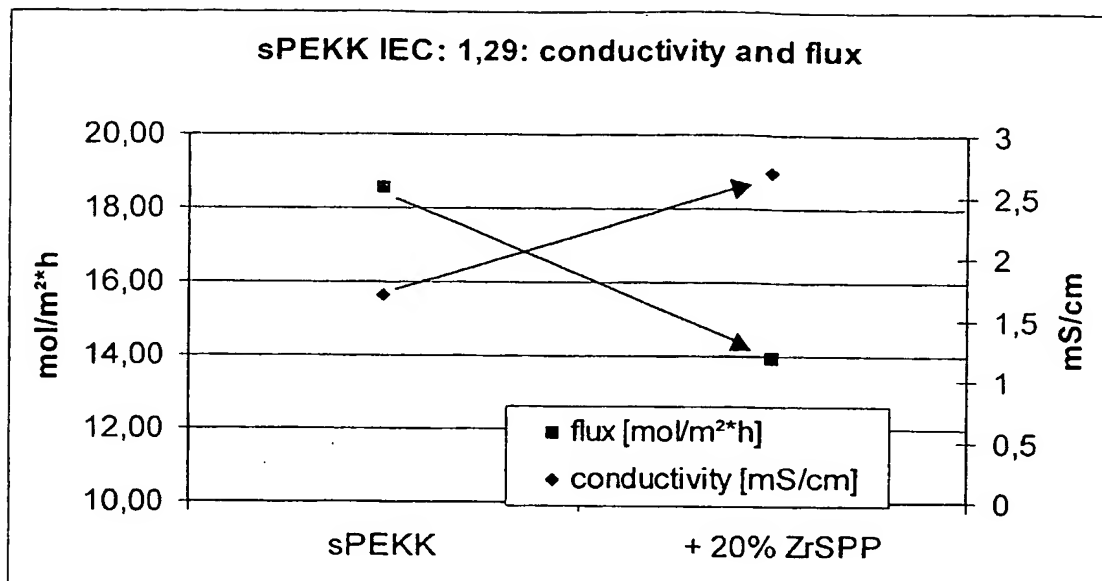


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Figure 5



5 Figure 7



5 Figure 9